Kinetics Studies of Two-Stage Soapless Emulsion Polymerization of Butyl Acrylate and Methyl Methacrylate

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SYNOPSIS

In this work, butyl acrylate (BA) and methyl methacrylate (MMA) were used as monomers and $K_2S_2O_8$ was used as the initiator to study the kinetics of two-stage soapless emulsion polymerization. The first stage of the reaction was to synthesize polyBA (PBA) seeds, and the second stage of the reaction was a seeded polymerization of MMA. The results showed that an increase of initiator concentration would increase the rate of polymerization and the number of polymer particles, but would decrease the size of the polymer particles and the weight-average molecular weight of the polymers. On the other hand, a decrease of the weight ratio of BA/MMA caused a decrease in the reaction rate and the weight-average molecular weight of the polymers in the second stage of the reaction. The morphology of emulsion particles was observed from transmission election microscopy (TEM). The polymer particles were very uniform in size and showed coreshell morphology with PBA as a core and polyMMA (PMMA) as a shell. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, seeded emulsion polymerization (or two-stage emulsion polymerization) was often used to synthesize core–shell polymer/polymer composites in industry. The core–shell polymer/polymer composites may include reinforced elastomers, high-impact plastics, toughened plastics, etc. For example, poly(butyl acrylate) (PBA)/(poly(methyl methacrylate) (PMMA) polymer composite could be made through seeded emulsion polymerization as follows: One of the monomers (BA or MMA) was synthesized as seeds in the first stage; then, the polymerization of the second monomer (MMA or BA) followed in the second stage.

The properties of the composite would vary with the BA/MMA ratio, polymerization conditions, and sequence of monomer fed. Many studies have focused on the kinetics of polymerization and the morphology of polymer particles of the polymer/polymer composites.[1,2]

There are many factors to control the kinetics and the morphology of polymer particles, such as the method by which the monomer is added to the system (batch, semibatch, or equilibrium swelling process)[3]; the sequence of the monomers fed into the system, the monomer ratio of the two stages, the hydrophilicity of monomers, surface tension, and molecular weight of the polymers[3–5]; the compatibility of the polymers[6]; and the properties of the initiators.[7]

In the last 20 years, emulsifier was used for seeded emulsion polymerization studies, and the morphology of polymer particles was observed by transmission electron microscopy.[3–5,8,9] Okubo et al. pointed out that the morphology of polymer particles could change with the molecular weight of polymers, viscosity of polymerization loci, and hydrophilicity of the two polymers.[8–10] Lee and Ishikawa synthesized two kinds of hydrophilic seeds that had high molecular weight and low molecular weight, respectively, and the morphology of particles changed with the molecular weight of polymers. The effect of monomer ratio in two stages on the particle morphology was also studied.[4]

Muroi and Hosoi studied the structure of core-shell latex particles. They pointed out that the polymer particles formed an inverted core–shell mor-

phology when the hydrophobic monomer of the second stage was polymerized in the presence of hydrophilic seeds.[11] Min et al. investigated the morphology of PBA–polystyrene (PS) composite latex particles and pointed out that the graft copolymers existing at the interface of polymers controlled the particle morphology.[3] Cho and Lee found that the oil-soluble initiator induced the inverted core–shell morphology and the water-soluble initiator would induce the inverted core–shell half-moonlike, sandwichlike, or core–shell morphology in the PMMA–PS composite latex system.[7]

So far, there have been few articles dealing with the synthesis of composite latex by the method of soapless emulsion polymerization. In this work, no emulsifier was added in our two-stage emulsion polymerization. BA and MMA were the monomers in the first and second stages, respectively. How the kinetics of polymerization would change with both the concentration of the initiator and the monomer ratio of the two stages was studied.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and butyl acrylate (BA) were distilled under a nitrogen atmosphere and reduced pressure prior to polymerization. Potassium persulfate ($K_2S_2O_8$), methanol, tetrahydrofuran, and hydroquinone were of analytical grade.

Ingredients for Polymerization

The Synthesis of Seed Latex (First Stage)

n-butyl acrylate (BA) (g)	30
Initiator ($K_2S_2O_8$) (g)	0.108–0.866
Deionized water (g)	820

The Synthesis of Composite Latex (Second Stage)

Seed emulsion (g)	780
Methyl methacrylate (MMA) (g)	2.75–110.1

Polymerization

The synthesis of seed emulsion was carried out in a 1 L reaction vessel fitted with a multinecked flanged top normally at a temperature of 70 ± 0.5°C. The polymerization did not use baffles. The stirring rate was controlled at 300 rpm. Nitrogen was bubbled through the reaction mixture and quantitative n-BA was added into the reactor. The aqueous solution of potassium persulfate ($K_2S_2O_8$) was added into

the reactor after the temperature of the system was 70°C, and the reaction of the first stage began.

The polymerization reaction of the first stage was complete over 1 h; then, the seed emulsion was quenched to room temperature. A quantitative MMA was added into the seed, and the seeds were swelled for 10 h. No new $K_2S_2O_8$ was added. Then, the reactor was heated in a water batch at 70°C and the reaction of the second stage (seeded polymerization) began. The half-life time of $K_2S_2O_8$ at 70 ± 0.5°C was 20.86 h.[12] Because the half-life time of the initiator was long, the initiator concentration in Stage 2 was approximately the same as that in Stage 1.

Conversion

At certain times during the polymerization, a sample of the emulsion latex was taken out of the reactor and poured into methanol with hydroquinone to stop the reaction. The precipitated polymers were filtered and washed with methanol and water several times and then dried in an oven. The conversions in the first and second stages were calculated based on gravimetric measurements.

Particle-size Distribution

The size distribution of polymer particles was measured by (1) photo correlation spectroscopy and (2) transmission electron microscopy.

By Photo Correlation Spectroscopy (PCS)

The samples taken from the reaction vessel had to be diluted with deionized water and were measured by PCS.

By Transmission Electron Microscopy (TEM)

One drop of the latex was placed onto a 2 μm Formvar film-coated grid and allowed to air-dry at room temperature, in a dust-free box, and was observed under the TEM at a 75 kV accelerating potential condition.

Particle Concentration

The particle concentration (N_p) was calculated as

$$N_p \cdot d_p \cdot 1 \cdot \frac{\pi \bar{D}^3}{6} = X \cdot M \cdot M_w \qquad (1)$$

i.e.,

$$N_p = 6 \cdot M_w \cdot M \cdot X / [\pi \cdot d_p (\bar{D} \cdot 10^{-7})^3]$$

where N_p is the particle concentration (1/L H_2O); M_w, the molecular weight of the monomer (g/mol); M, the monomer concentration (mol/L H_2O); d_p the polymer density (g/cm^3); $\bar{D}$, the number-average diameter of particles measured by TEM (nm); and X, the conversion.

Molecular Weight Determination

The weight-average molecular weight of the polymers was determined with a Shodex RI gel permeation chromatograph (GPC Model SE-61) on dry samples dissolved in tetrahydrofuran.

Observation of Particle Morphology

The latex particles in the seeded polymerization were ultramicrotomed. The sections of the latex particles were observed under the TEM.

RESULTS AND DISCUSSION

Conversion

Figures 1 and 2 shows the curves of conversion vs. time at different initiator concentrations in the first and second stages of the reaction, respectively. An increase of the initiator concentration would increase the rate of polymerization.

Figure 3 shows the temperature profile of the reaction at different weight ratios of BA/MMA in the second stage of the reaction. When the ratio of BA/MMA was smaller, it meant that a larger amount of MMA was fed into the reactor at room temper-
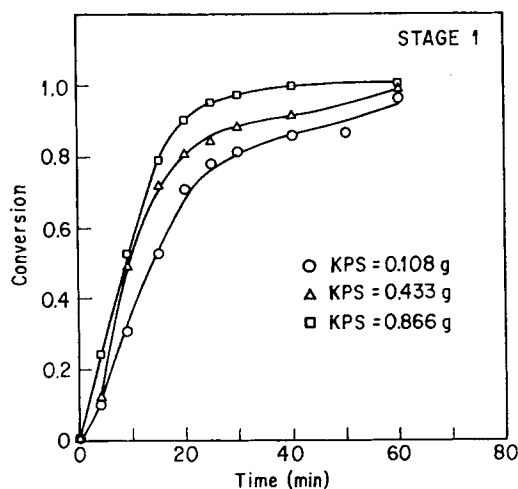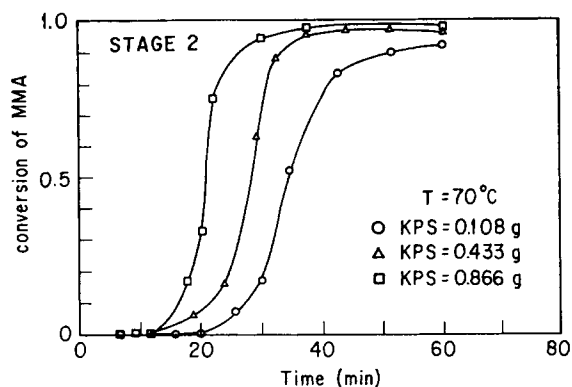

Figure 2   Conversion vs. time at different initiator concentrations (stage 2); BA/MMA = 1/2.

ature. Right before the second stage of the reaction, more energy was required to heat up the reaction mixture, so the temperature of the reaction system would go up more slowly in the initial period of reaction. But it would reach a higher temperature latex because more reaction heat would release at a higher concentration of the MMA monomer. Figure 4 shows the effect of the BA/MMA ratio on the conversion of the reaction in the second stage of the reaction. When the ratio of BA/MMA was smaller, the rate of polymerization would be slower initially but speed up later, corresponding to its temperature profile as seen in Figure 3.

Concentration of Monomers in Polymer Particles ($[M]p$)

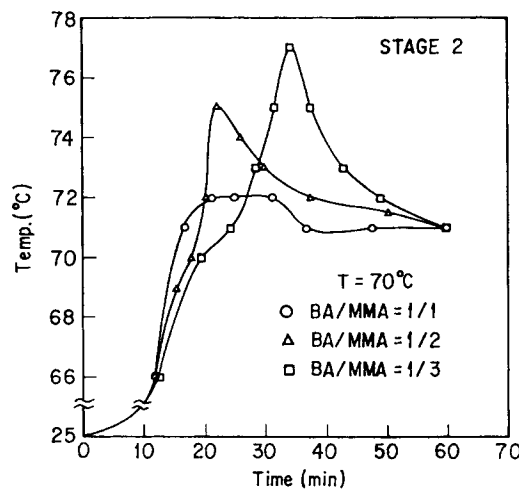The relation between conversion and concentration of the monomer in polymer particles was observed

Figure 1   Conversion vs. time at different initiator concentrations (stage 1).

Figure 3   Temperature vs. time at different BA/MMA ratios (stage 2).
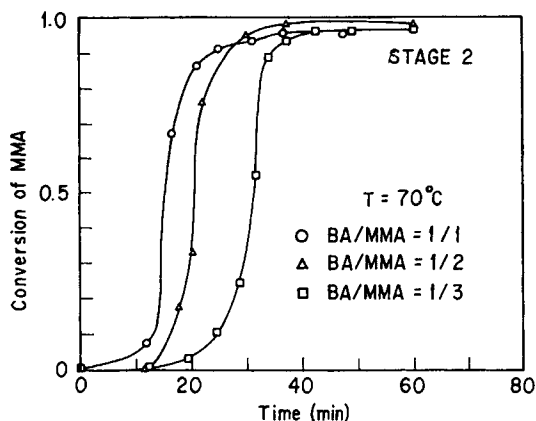
Figure 4 Conversion vs. time at different BA/MMA ratios (stage 2).

Figure 6 Particle size (number-average diameter) vs. time at different initiator concentrations (by PCS) (stage 1).

from experiments.[13] The result is showed in Figure 5. When the conversion was under 50%, the concentration of the monomer in the polymer particles was kept at 4.2 mol/L. It meant that the monomers diffused into the polymer particles very quickly whenever monomer droplets existed in the reaction system, so the concentration of the monomer in the polymer particles was retained at saturated concentration. When the conversion was above 50%, monomer droplets disappeared and an increase of the conversion would decrease the concentration of the monomer in the polymer particles.

Size of Polymer Particles

Measured by PCS

In the First Stage. Figure 6 shows the plots of average particle size vs. time at different initiator concentrations in the first stage of the reaction. An increase of reaction time would increase the size of
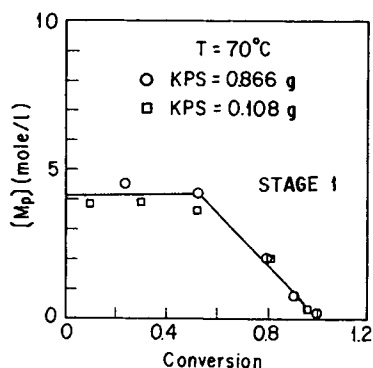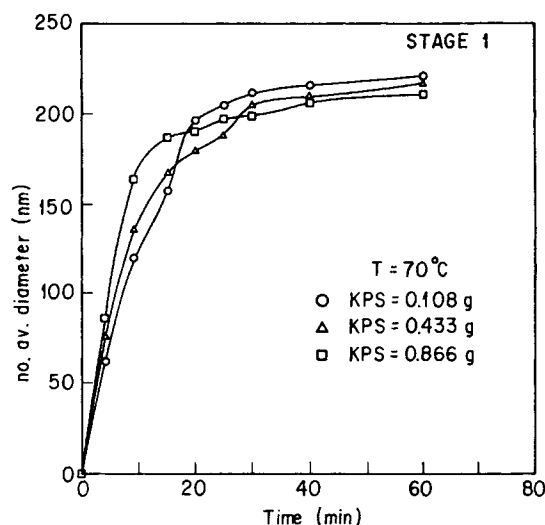
the polymer particles first, but when the monomer droplets disappeared and the polymer particles were hard enough to avoid coagulation, the size of the polymer particles would not increase any more. When the system contained more initiator, the particles would grow faster initially but level off at a smaller size. As mentioned above, more initiator would generate more polymer particles in the system, so the final size of the polymer particles was smaller at a fixed concentration of monomers.

In the Second Stage. Figure 7 shows the plots of average particle size vs. time at different weight ratios of BA/MMA in the second stage of the reaction. A decrease of the BA/MMA ratio would increase the shell (PMMA) layer, so the size of polymer particles would be larger at the end. Theoretically, a 1/1 ratio of MMA to BA seed will cause
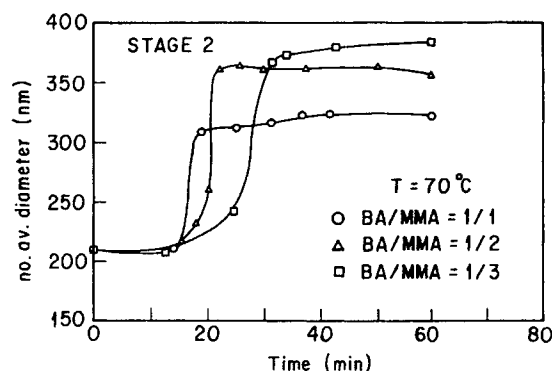

Figure 5 Concentration (mol/L) of BA in the polymer particles as a function of conversion.

Figure 7 Particle size (number-average diameter) vs. time (by PCS) at different BA/MMA ratios (stage 2).

particles to grow from 210 to about 261 nm, the 1/2 ratio from 210 to 300 nm, and the 1/3 ratio from 210 to 330 nm. But the experimental values measured by PCS were about 310, 350, and 380 nm at the end. Because the standard deviation measured by PCS was about 60 nm, if we considered the experimental deviation, a little flocculation might take place, but it was not significant. Figure 8 shows the effect of initiator concentration on the average particle size in the second stage of the reaction. An increase of initiator concentration would decrease the final size of polymer particles with the same trend as that in the first stage of the reaction.

Measured by TEM

In the First Stage. Because the PBA particles were soft, the particles would melt when observed by TEM. Therefore, we did not use TEM to measure the size of the PBA particles.

In the Second Stage. The size of the polymer particles could also be observed by TEM and are shown in Figure 9. There were about 50 particles measured via TEM to determine the particle size. The size of the polymer particles was rather uniform. A decrease of the BA/MMA ratio would increase the size of the polymer particles as shown in Figure 9(1) and (2). An increase of initiator concentration would decrease the size of the polymer particles, as shown in Figure 9(2) and (3).

Particle Concentration

Because the PBA particles were too soft to be measured by TEM, we used PCS instead of TEM to measure the size of the PBA particles. The following equation relates the size of the particles by PCS to the size of the particles by TEM:
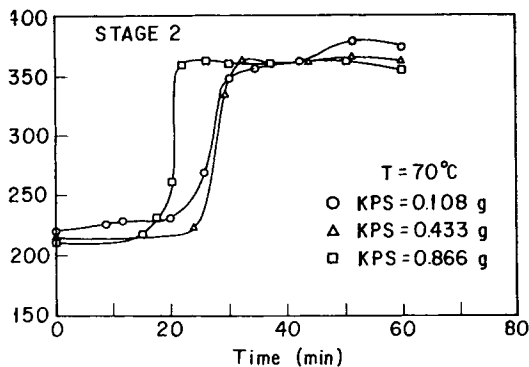
Figure 8 Particle size (number-average diameter) vs. time (by PCS) at different initiator concentrations (stage 2), BA/MMA = 1/2.

$$\frac{\pi}{6}(\bar{D}_{\text{pcs}} \times 10^{-7})^3 - V_M = \frac{\pi}{6}(\bar{D}_{\text{TEM}} \times 10^{-7})^3$$

$$V_M = \frac{\pi}{6}(\bar{D}_{\text{pcs}} \times 10^{-7})^3 \frac{[M_p]}{1000}\frac{M_w}{\rho_M} \quad (2)$$

$$\Rightarrow \bar{D}_{\text{TEM}} = (\bar{D}_{\text{pcs}} \times 10^{-7}) \times \sqrt{1 - \frac{[M_p]M_w}{1000\rho_M}} \quad (3)$$

where V_M is the monomer volume in the polymer particle (cm^3); $[M_p]$, the monomer concentration in the polymer particles as shown in Figure 5; $\bar{D}_{\text{pcs}}$, the average diameter of the particles measured by PCS (nm); $\bar{D}_{\text{TEM}}$, the average diameter of the particles measured by TEM (nm); M_w, the molecular weight of the monomer (g/mol); and ρ_m, the monomer density (g/cm^3).

Once the particle size by TEM was determined from eq. (3), then the particle concentration could be estimated by eq. (1). As shown in Figure 10, the particle number of the reaction system decreased with increasing reaction time and reached a steady value in each run of experiments. Initially, the polymer particles were swollen with monomers, so the polymer particles were soft and easily coagulated with each other. Moreover, the charge density of the particle surface decreased with increasing size of the polymer particles, so the number of particles decreased continuously during the polymerization through coagulation. As the reaction proceeded, in the later period of the reaction, particles became harder and no more coagulation among particles occurred, and then the particle concentration would reach a steady value. It also shown in Figure 10 that an increase of initiator concentration would increase the particle number in the system.

Average Molecular Weight of Polymers

Weight-average Molecular Weight of PBA (First Stage)

Figure 11 shows the curves of the weight-average molecular weight of PBA vs. conversion in the first stage of the reaction. The weight-average molecular weight of PBA increased first and then decreased with increasing conversion. Two factors might influence the molecular weight of the polymers: gel effect and coagulation. The gel effect would increase the molecular weight of the polymers, but the coagulation among particles would increase the number of radicals in one particle, which would reduce the molecular weight of the polymers. On the other hand, an increase of initiator concentration would
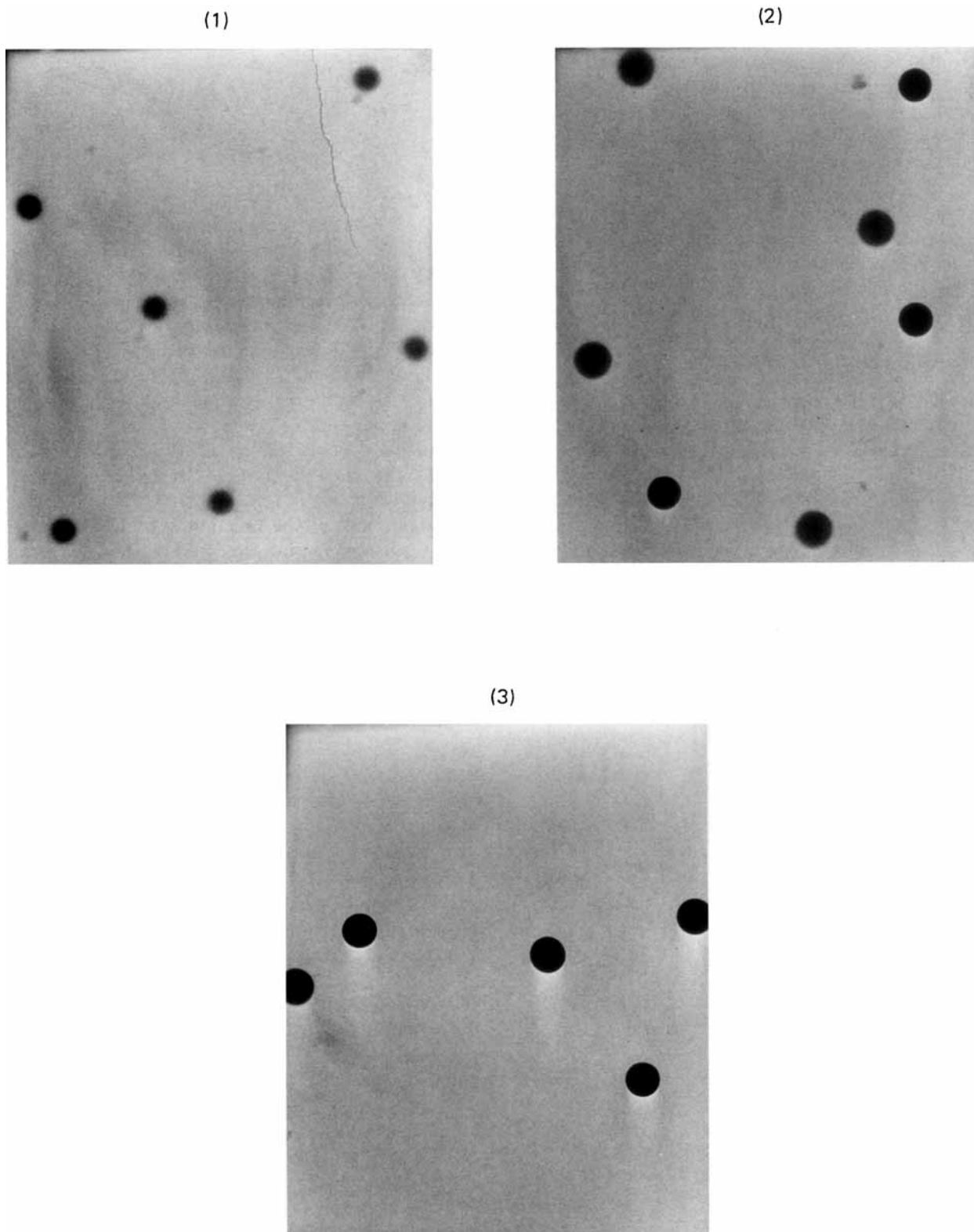
(1)

(2)

(3)

Figure 9   TEM photographs of polymer particles (magnification = ×20K) stage 2; time = 60 min. (1) BA/MMA = 1/1, $k_2S_2O_8$ = 0.866 g; (2) BA/MMA = 1/3, $k_2S_2O_8$ = 0.866 g; (3) BA/MMA = 1/3, $k_2S_2O_8$ = 0.108 g.
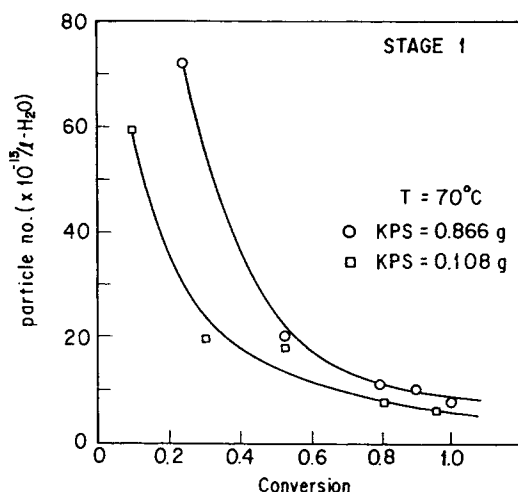
Figure 10 Number of particles (1/L H$_2$O) vs. conversion at different initiator concentrations (stage 1).

Figure 12 Weight-average molecular weight of PMMA vs. time at different initiator concentrations (stage 2).

decrease the weight-average molecular weight of the polymers, as expected.

Weight-average Molecular Weight of PMMA (Second Stage)

In the second stage of the reaction, the polymers that we obtained contained both PBA and PMMA, so a mixed Q factor used in our calculation of the GPC curve was required:

$$\frac{1}{Q_{mix}} = \frac{QW_{PBA}}{Q_{PBA}} + \frac{W_{PMMA}}{Q_{PMMA}} \qquad (4)$$

where Q_{mix} is the mixed Q factor of PBA and PMMA; Q_{PBA}, the Q factor of PBA (assume $Q = 41$); Q_{PMMA},

the Q factor of PMMA ($Q = 23$); W_{PBA}, the weight fraction of PBA in the polymers; and W_{PMMA}, the weight fraction of PMMA in the polymers.

Then, the weight-average molecular weight of the polymers containing both PBA and PMMA was calculated as

$$M = G \times \frac{Q_{mix}}{Q_{ps}} \qquad (5)$$

where G is the weight-average molecular weight measured by GPC based on PS, and G_{ps}, the Q factor of PS.

The weight-average molecular weight of PMMA (M_{PMMA}) was calculated as

$$M = W_{PBA}M_{PBA} + W_{PMMA} + M_{PMMA}$$

$$\Rightarrow M_{PMMA} = \frac{(M - W_{PBA}M_{PBA})}{1 - W_{PBA}} \times \frac{Q_{PMMA}}{Q_{ps}} \qquad (6)$$

where M_{PBA} is the weight-average molecular weight of PBA at the end of the first stage of the reaction.

Figure 12 shows the relation of the weight-average molecular weight of PMMA vs. time at different initiator concentrations in the second stage of the reaction. A decrease of initiator concentration would increase the weight-average molecular weight of PMMA, as we found in the first stage of the reaction.

An increase of the BA/MMA ratio would increase the weight-average molecular weight of PMMA, as shown in Figure 13. The reason was that when the reaction system contained more MMA monomers the gel effect was less significant and the living polymer chains were easy to terminate; so the weight-

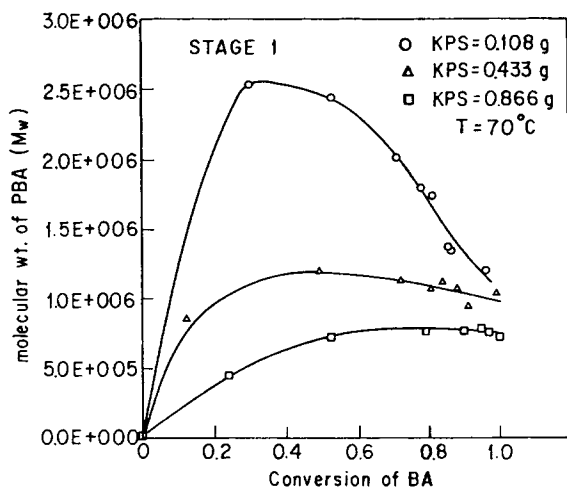**Figure 11** Weight-average molecular weight of PBA vs. conversion at different initiator concentrations (stage 1).

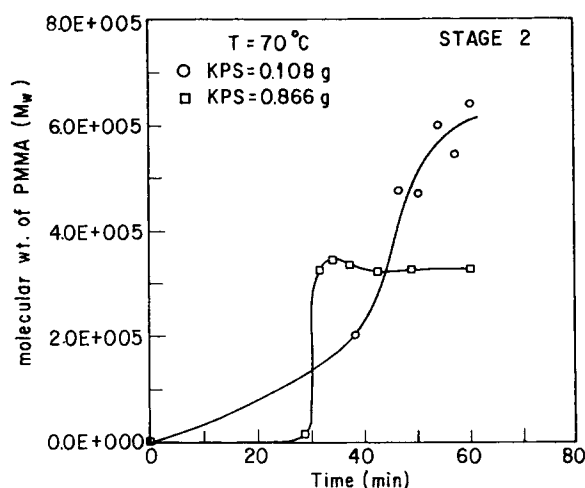average molecular weight of PMMA was lower than in the system containing fewer MMA monomers.

Morphology Observation of Latex Composite Particles

The latex particles were ultramicrotomed. The sections of the latex particles were observed under the TEM. The core–shell morphology is shown in Figure 14. The core was PBA and the shell was PMMA.

CONCLUSION

In the reaction of the first stage, an increase of the concentration of initiator would increase the rate of polymerization and increase the particle concentration, but would decrease the size of polymer particles and decrease the weight-average molecular weight of the polymers. In the reaction of the second stage, a decrease of the BA/MMA ratio would decrease the initial rate of polymerization and would decrease the weight-average molecular weight of PMMA, but would increase the size of the polymer particles at the end of the reaction. The concentration of monomer in the polymer particles retained a saturated concentration, 4.2 mol/L, when the concentration was below 50%. The saturated concentration was independent of the concentration of the initiator and concentration of the monomer. The latex particles were rather uniform during the polymerization. The morphology of the latex particles showed a core–
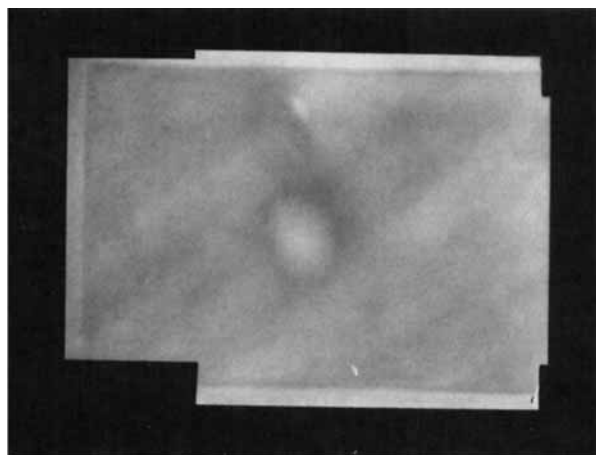

Figure 14 TEM photographs of latex composite particles $K_2S_2O_8$ = 0.866 g, BA/MMA = 1/3 reaction time = 60 min.

shell structure: The core was PBA and the shell was PMMA.

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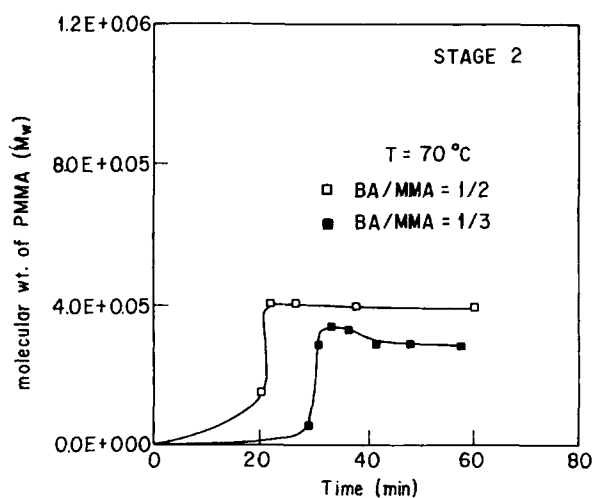
Figure 13 Weight-average molecular weight of PMMA vs. time at different BA/MMA ratios (stage 2).